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Pressure-dependent product distribution of citral hydrogenation over micelle-hosted Pd and Ru nanoparticles in supercritical carbon dioxide

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Abstract

In situ synthesis and testing of Ru and Pd nanoparticles as catalysts in the presence of ammonium perfluorohydrocarbo-carboxylate surfactant in supercritical carbon dioxide were carried out in a stainless steel batch reactor at 40 °C over a pressure range of 80–150 bar CO_2/H_2. Direct visualization of the formation of a supercritical phase at above 80 bar, followed by the formation of homogeneous microemulsions containing dispersed Ru nanoparticles and Pd nanoparticles in $scCO_2$ at above 95–100 bar, were conducted through a sapphire window reactor using a W_0 (molar water to surfactant ratio) of 30. The synthesised Ru and Pd nanoparticles showed interesting product distributions in the selective hydrogenation of organic molecules, depending critically on the density and polarity of the fluid (which in turn depends on the pressure applied). Thus, selective hydrogenation of the citral molecule, which contains three reducible groups (aldehydes and double bonds at the 2,3 and 6,7 positions), is feasible as a chemical probe.

Keywords: Citral hydrogenation; Micelle-hosted Ru nanoparticle; Supercritical carbon dioxide; Citronellal selectivity

1. Introduction

Since the early 1990s, an increasing concern about discharge from chemical industries has led to the reassessment of various existing chemical processes. Particular attention has been paid on the use of supercritical carbon dioxide ($scCO_2$) to replace organic solvent because it is nontoxic, nonflammable, inexpensive, inert, and environmentally benign [1]. Pioneering researchers have focused on the advantages of using $scCO_2$ in polymer synthesis and processing and have achieved enormous success [2,3]. Encouraged by these promising results, $scCO_2$ is being explored as a new medium for catalytic hydrogenation of organic molecules. Higher reaction rates and excellent enantioselectivity have been claimed [4–8]. Catalytic fixation of CO_2 in its supercritical state, in which CO_2 is used as solvent and reactant, has also been reported [9,10]. Many enzymatic reactions taking place in this fluid are currently under investigation [11]. The medium is generally shown to be effective for a wide range of reactions, including hydroformylation [12,13] and oxidation [14–19], because of its intrinsically high miscibility with other gases, high diffusivity, and high mass transfer coefficient [1]. But little attention has been paid to the pressure effect on reaction selectivity, despite the fact that the fluid may offer some tunable properties leading to desirable products.

Consequently, we have investigated hydrogenation of the citral molecule, which contains three reducible groups (aldehydes and double bonds at the 2,3 and 6,7 positions) as a chemical probe for this new solvent medium. The economic importance of selective hydrogenation reactions of α,β-unsaturated aldehydes has been emphasized [20,21], because some partial hydrogenated products are widely used in the production of pharmaceuticals, fragrances, and perfumes [22]. In the literature, selective hydrogenation of these compounds has been studied extensively over a wide range of catalysts, including promoted and unpromoted metals/alloys [23–25], metal oxides [26,27], microporous supports [28], and polymer fibre catalysts [29] in both liquid [21,30–32] and vapour [33,34] phases. It has been empirically shown that the selectivity of the reaction can depend on some key parameters, including the nature of the metal and particle size [35], catalyst support [36–38], and

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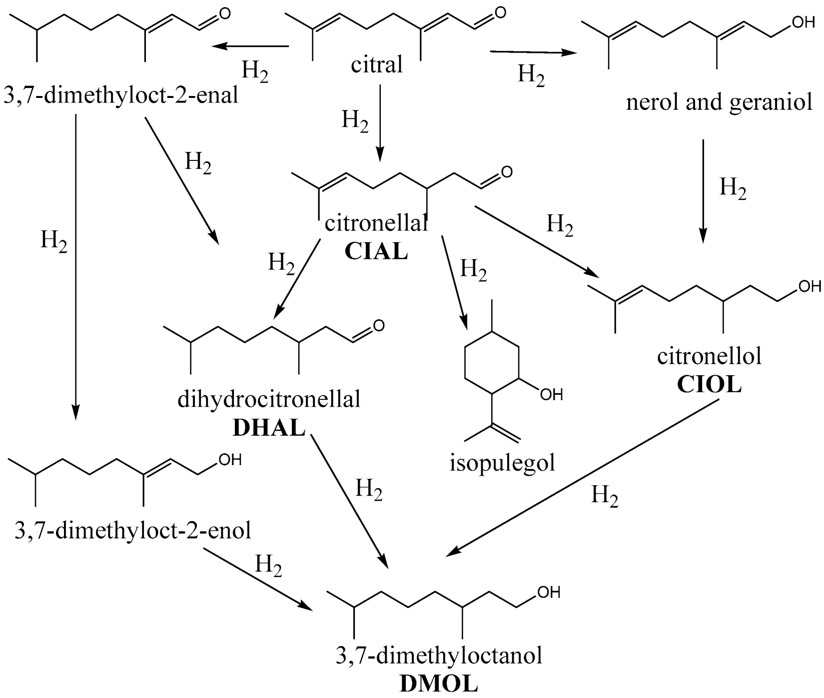

Scheme 1. Reaction pathways of citral hydrogenation.

type of promoters/additives [38–40] used; however, a systemic control in reaction selectivity by these parameters leading to tunable properties has not yet been achieved. Citral molecule is one interesting model compound for hydrogenation because it contains both conjugated and isolated double bonds as well as a carbonyl group; thus numerous partially hydrogenated products can be synthesised, depending on the selectivity of the hydrogenation reaction (see Scheme 1). Hydrogenation of the citral molecule over Pd nanoparticles with and without support materials [41,42] in $scCO_2$ has also been reported.

In the present paper we report a detailed study of pressure effect on citral hydrogenation by micelle-hosted Ru and Pd nanoparticles in supercritical carbon dioxide following our previous preliminary works on the Pd system [43,44]. Two fundamental issues are of particular importance in this paper: to carry out direct visualisation of surfactant/metal system in $scCO_2$ through a sapphire window reactor at different pressure ranges, and to investigate the pressure effect affecting product selectivity in hydrogenation. Both of these issues are fundamentally important in terms of the future development of this new type of catalysis.

2. Experimental

Citral, decane, perfluorotetradecanoic acid, and ammonia solution in methanol were supplied from Aldrich, and cyclohexane and methanol were supplied from Fischer Scientific. All of these reactants were used without any further purification. Palladium chloride, ruthenium chloride, unsupported (naked) palladium, and ruthenium nanoparticles were provided by Johnson Matthey.

2.1. Synthesis of the fluorinated ammonium surfactant

Perfluorotetradecanoic acid, $CF_3(CF_2)_{12}COOH$, was dissolved in methanol under stirring at the temperature of 40 °C. The synthesis, purification, and characterisation of Co(II) perfluorotetradecanoate salt were described previously [45]. Using a similar methodology, a five-fold excess of 2.0 M ammonia solution in methanol was added to the acid solution, and the mixture was maintained at 40 °C under vigorous stirring for 24 h. The generated $CF_3(CF_2)_{12}COO^-NH_4^+$ was collected as a dried powder by evaporating off the solvent and excess ammonia at 60 °C overnight. A slightly yellow-coloured solid was obtained. Purity of the synthesised material was confirmed by elemental analysis; the formation of ammonium salt could also be monitored by FTIR. A clear shift in wave number at the C=O stretching absorption region was observed when the ammonium salt was formed (from 1768 to 1683 cm^{-1}). To ensure that no acid was left over in the ammonium salt, the absence of an acid absorption peak was particularly noted.

2.2. Visualisation of the microemulsion through a sapphire window reactor

Experiments were carried out in a ca. 30-mL stainless steel Parr reactor equipped with two high-pressure transparent sapphire windows with the window separation of ca. 4.5 cm. Appropriate amount of reactants, palladium nitrate, surfactant, and water were introduced in the reactor to create the same conditions (40 °C and 150 bar overall pressure) as a 300-mL reactor in which catalysis was performed. The only difference between the two reactors was in the stirring; the small reactor was stirred using a magnetic stirrer at the bottom of the reactor.